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Tritium behavior in lithium ceramics

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Abstract

Tritium is the principal fuel for future fusion power reactors. Unfortunately, tritium is not available naturally and so must be produced through transmutation of lithium. The current approach to fusion reactor breeder blanket design is to place lithium-containing ceramics in a blanket module that surrounds the fusion plasma. These materials have performed well in numerous in-pile experiments, showing good thermal stability and good tritium release characteristics. Tritium release is particularly facile when an argon or helium purge gas containing hydrogen, typically at levels of about 0.1%, is used. However, the addition of hydrogen to the purge gas imposes a penalty when it comes to recovery of the tritium produced in the blanket. Optimizing tritium release while minimizing the amount of hydrogen necessary in the purge gas requires a detailed understanding of the tritium release process, especially the interactions of hydrogen with the surface of the lithium ceramic. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium, in some form, appears to be the only material suitable for breeding tritium in a fusion reactor, and it is imperative that sufficient supplies of tritium fuel be available to sustain the D/T fusion reaction. Lithium-based ceramics have long been recognized as promising tritium-breeding materials for fusion reactor blankets [1]. These materials exhibit excellent tritium release and thermophysical and thermomechanical characteristics. Probably the most important qualification for a candidate ceramic breeder material is its ability to withstand the rigors of long-term irradiation at high temperature and large temperature gradients. Because of their overall desirable properties, lithium-containing ceramics are recognized as attractive tritium breeding materials for fusion reactor blankets. Indeed, their inherent thermal stability and chemical inertness are significant safety advantages.

To secure this tritium supply, current fusion reactor designs contain a breeder blanket for production of tritium. The tritium breeder blanket in the fusion reactor serves two primary functions: breeding tritium and converting the released energy into sensible heat, both of which are critical to fusion power development. In numerous in-pile experiments on tritium release, it has been shown that hydrogen enhances tritium release from lithium ceramics. Tritium release is particularly facile when an argon or helium purge gas containing hydrogen, typically at levels of about 0.1%, is used. However, the addition of hydrogen to the purge gas imposes a penalty when it comes to recovery of the tritium produced in the blanket. In particular, a large amount of hydrogen in the purge gas is likely to require a multiple-stage tritium purification unit for isotope separation. Optimizing tritium release and recovery while minimizing the amount of hydrogen necessary in the purge gas requires a deeper understanding of the tritium release process, especially the interactions of hydrogen with the surface of the lithium ceramic. Candidate ceramics such as Li_2O, $LiAlO_2$, Li_2TiO_3, Li_2ZrO_3, and Li_4SiO_4 are being considered for their suitability as acceptable blanket materials and the source of tritium for the fusion reactor.

This paper discusses ongoing research on the thermodynamic behavior and the irradiation behavior of lithium ceramics, the tritium transport and release process, and the theoretical studies designed to improve our understanding of the tritium–hydrogen reactions on the surface of the ceramic.

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2. Thermodynamic properties

Of the many areas of research that are important in the development of fusion energy, the recovery of tritium from the lithium-containing breeder blanket is one that involves considerable thermodynamic analysis. In the lithium ceramic breeder blanket, lithium is readily converted to tritium after reacting with a neutron. With the addition of hydrogen to the helium purge gas, the bred tritium is readily recovered from the blanket as HT and HTO. Within the solid, tritium may be present as the OT^- ion, which may also participate in transport of lithium. The pressure of LiOT (g), HTO (g), or T_2O (g) above Li_2O (s) is the same as that for reactions involving hydrogen. In most of the experiments described here, hydrogen was used instead of tritium.

The initial effort to characterize the behavior of tritium in lithium ceramics was to determine the solubility of LiOH in Li_2O from which many thermodynamic parameters can be determined. Measurements were made of the solubility of hydroxide in Li_2O and of the vaporization of hydroxide from Li_2O into a helium gas stream containing varying amounts of H_2O vapor [2–4]. The solubility data were transformed into activity coefficients that enabled correction for non-ideality of solutions of hydroxide in the Li_2O system [5]. A general conclusion from this effort was that the behavior of ceramic breeders would be strongly dependent upon the oxygen activity prevailing in the system. Oxygen activity controls the form of the released tritium, i.e., either the oxidized or reduced form, the amount of tritium retained in the condensed phase, and the amount of blanket transported as LiOH/LiOT vapor. The sensitivity to oxygen activity in determining either oxidized or reduced forms of released tritium is such that nominally 'pure' sweep gas containing only parts per million of oxygen and/or H_2O will be strongly on the oxidizing side. If oxygen activity is reduced sufficiently, it may be possible for hydride to become an important species in the condensed phase [6].

Thermodynamic calculations have been carried out for the condensed and gaseous phases of candidate lithium ceramics. This effort enabled a comparison of the thermochemical characteristics of these materials. This comparison was based upon the amounts of tritium retained in the condensed phase, the amount of tritium in the gas phase, the amount of lithium vaporized, and the amount of LiOH vapor transport. The calculations suggest that the performance of $LiAlO_2$ is better than that of Li_2O, which is better than that of Li_4SiO_4, i.e., exhibits lower lithium loss. At high temperatures and very low oxygen activities, Li_2O is better than $LiAlO_2$ with respect to concentration of tritoxide in the condensed phase [5].

Partial pressures of the different species over the ceramics have been expressed as a function of temperature, showing that higher lithium vapor pressures exist for materials of higher lithium content. Measurements made using a carrier gas stream of varying H_2O partial pressure showed that moisture enhances the volatility of Li_2O as LiOH vapor. Results are derived in terms of the equilibrium constants for the reaction Li_2O (s) + H_2O (g) = 2LiOH (g) [7].

The transport of lithium by vaporization of LiOH (g) from lithium ceramics poses a constraint on the maximum operating temperature of the breeder blanket that may limit operation to ~1000 K. Experimental measurements have shown that, depending on temperature, moisture partial pressure and proximity of structural steels, the lithium transport process is complex [8]. For conditions wherein the candidate ceramic (e.g., Li_2O) is 'free standing', the lithium vaporization is controlled by the Li_2O/H_2O system thermodynamics; that is, lithium transport, as LiOH (g) increases with increasing temperature and higher partial pressures of moisture. Near to the stainless steel structural materials, there is an added chemical-potential driving force due to the formation of Li_2CrO_2, $LiFeO_2$, and $LiNiO_2$ [8]. The transport of LiOH (g) to the stainless steel is driven by the concentration gradient of LiOH (g) from that at the candidate ceramic surface and that at the steel surface. This gas–solid reaction may become important for blanket designs where the structural steel is very close to the lithium ceramic.

An operating issue in the performance of ceramic breeder materials is tritium inventory. Generally, it is assumed that the tritium inventory of the ceramics will depend upon gas–solid equilibration (bulk solubility, adsorption on the grain surface) and on kinetic processes (diffusion in the grain, desorption from the grain surface). Tritium desorption has been identified as important in determining the kinetic processes and the mechanism of tritium release from ceramic breeder materials. If tritium release is slow, the result will be an increase in the tritium inventory in the blanket that is unacceptable from both an economic and safety viewpoint. (~1000 K).

3. Irradiation performance

A critical factor in evaluating candidate lithium ceramics is their performance under neutron irradiation. Such experiments test a material's resistance to fracture, swelling and changes in thermophysical properties, and enables examination of its tritium release characteristics. Recent laboratory tests indicated excellent tritium release behavior of Li_2ZrO_3 and Li_2TiO_3 to low temperatures [9,10]. Also, tritium diffusivity in single-crystal Li_2TiO_3 was measured over the temperature range 352–1103°C to provide baseline properties for tritium transport [11]. While its role has yet to be fully understood, the importance of hydrogen in the helium purge gas to the tritium recovery process has been amply demonstrated in both laboratory and in-reactor tests. Helium generated in ceramic breeder materials during neutron irradiation may have a significant impact on the durability of candidate ceramics. Helium diffusion in the grains and release from closed pores was recently examined for Li_2O [12].

A number of in-reactor tests were conducted in the HFR (Petten, NL), NRU (Chalk River, CA), and FFTF (Richland, WA) reactors.

The EXOTIC-6 irradiation test at HFR Petten focused on tritium release studies of candidate ceramics in pellet and pebble configurations [13]. A tritium residence time of one day, in He + 0.1% H_2 purge gas, was found at ~400°C for 76% TD $LiAlO_2$ pellets, at ~350°C for 94% TD Li_4SiO_4 pebbles, and at ~250°C for 73% TD Li_2ZrO_3 pellets. In the EXOTIC-7 irradiation test, 50% ^6Li-enriched Li_2ZrO_3 and $LiAlO_2$ pellets and Li_2ZrO_3 and Li_4SiO_4 pebbles were irradiated to 6–18% burnup [14,15]. Pellet stacks and pebble beds remained essentially intact during irradiation. Tritium inventory measurements confirmed values obtained from previous EXOTIC tests. Tritium release from Li_2ZrO_3 ceramic was excellent. Tritium residence times were not affected by lithium burnup. Postirradiation examination of the mixed Be–Li_4SiO_4 pebble bed showed implanted tritium in beryllium when lithium ceramic and beryllium were intimately mixed. The tritium inventory was found to be very high, with the smaller pebbles having the largest inventory. The first phase of the EXOTIC-8 experiment (June 1997) focused on Li_2TiO_3 pebbles. The second phase will include pebble specimens of Li_2TiO_3 and Li_2ZrO_3. Irradiation capsules can accommodate ~50% ^6Li enriched specimens of Li_2TiO_3 and Li_4SiO_4, allowing them to achieve lithium burnups of 7–10% representative of DEMO end-of-life performance.

The CRITIC-II irradiation test in the NRU reactor at Chalk River focused on the irradiation of Li_2ZrO_3 pebbles [16]. The temperature gradient in the pebble bed ranged from 200°C at the outer edge to ~1100°C at the center. The final burnup achieved 0.5% total lithium after 272 full power days (FPD). Postirradiation examination of the pebbles indicated very low tritium inventory, except at the lowest temperature. Tritium inventory ranged from ~5 to 0.01 wppm for the operational temperature range. Lifetime tritium release from Li_2ZrO_3 pebbles showed very low tritium inventory and excellent performance at the target burnup. Currently in progress is the CRITIC III test, which focuses on the irradiation of Li_2TiO_3 pebbles; a lithium burnup of about 0.5% is expected to be achieved. The tritium release behavior of Li_2TiO_3 pebbles in CRITIC III is comparable to that of Li_2ZrO_3 pebbles in CRITIC II.

For the BEATRIX II irradiation test in the FFTF fast reactor at Richland, burnups in excess of 5% were achieved. The Li_2O solid pellets and the Li_2ZrO_3 pebble bed operated at a centerline temperature of ~1000°C and edge temperature of ~400°C. In spite of these extreme conditions, Li_2O and Li_2ZrO_3 performed very well; Li_2O exhibited good tritium release throughout the irradiation, and this was confirmed by a measured very low tritium inventory of 0.06 wppm [17]. Ceramic integrity was maintained during irradiation to 5% burnup, although some structure changes and swelling occurred along with a very small loss of lithium [17,18]. For Li_2ZrO_3 at this burnup level, tritium release was constant, with no indication that second phase formation degrades tritium release behavior. Material fracture was not observed in the ceramic breeder material. Lifetime tritium release of Li_2ZrO_3 pebbles showed very low tritium inventory and excellent performance of pebbles up to 1100°C for ~200 FPD [19].

4. Tritium transport and release

Tritium transport and release from a lithium ceramic breeder material is a complex process involving diffusion in the grain, trapping, grain boundary diffusion, surface reactions, desorption, and molecular diffusion in the gas phase. The liberation of tritium from neutron-irradiated lithium ceramics involves the diffusive motion of the tritium atom within the solid and its subsequent release from the ceramic surface [20–24]. From these studies, it was generally assumed that diffusion was the rate-limiting mechanism for tritium transport and release from the ceramic, and the rate constants for tritium diffusion were determined. Interestingly, tritium diffusivity values ranging over six orders of magnitude were reported. However, in other studies [25–31], it was shown that the rate-controlling step changed from surface phenomena to diffusion as the grain size of the specimen increased and as temperature increased. In order to address tritium release issues, one needs a firmer understanding of the mechanism through which hydrogen enhances tritium release. Generally, the method for determining the diffusion and desorption rate constants has been to observe tritium release from the ceramic and analyze the time dependence of the release process. The data are then analyzed using a diffusion, desorption, or a mixed diffusion–desorption model. A full understanding of these processes is critical to achieving an efficient production of tritium fuel to sustain the fusion reaction.

4.1. Tritium transport in the bulk

Bertone [32] may have been the first to address the boundary conditions that define whether bulk diffusion or surface desorption is the rate-limiting step in tritium release. This study indicated that tritium release is controlled by the following: (1) diffusion of tritium through the crystal when the dimensionless group ak/D is >10, 2) desorption of tritiated water from the crystal surface when ak/D is <1, and (3) a combination of these processes when $1 < ak/D < 10$, where a is a characteristic crystal size, k is the governing desorption rate constant, and D is the governing diffusion coefficient. As both the diffusion coefficient and the desorption rate constant are temperature dependent, this approach indicates that the form of the rate-controlling mechanism depends primarily on crystal size and release temperature. These theoretical studies were followed by the experimental work of Quanci [33] on single-crystal Li_2O and this work more clearly demonstrated the boundary conditions as outlined by Bertone.

Too often in experimental studies, the initial release behavior does not follow the prescribed mathematics due to time delays in the recorded tritium release or because of the vagaries in the mathematics and the experimental apparatus. Verrall [34] established a more rigorous methodology for the Bertone [32] approach when he identified the need to initiate analysis at a particular time in the tritium release process. In practice, the release rate of tritium will never follow the diffusion-controlled relation at short times, even when the release of tritium is controlled by diffusion, because the formula diverges (goes to infinity) at $t = 0$. Also, ionization chambers and proportional counters have a relatively large internal volume that contains the tritium that is being measured. As the tritium enters the chamber, the tritium concentration in the chamber increases from zero to a finite maximum and then decreases. Under these conditions, the measured release rate does not follow the relation $\partial \ln (f)/\partial \ln (t) = 1/2$, especially at short times. Surprisingly, no matter what the shape of the release curve and no matter what point along the curve is selected as t goes to zero, the relation $\partial \ln (f)/\partial \ln (t)$ was found to be equal to 1. Although this limit is 1 for all tritium release curves, diffusion and desorption control can still be distinguished by examining $\partial \ln (f)/\partial \ln (t)$, not in the limit as t goes to zero, but for longer times, i.e., many times the detector time constant. Thus, the shape of the logarithmic derivative over long times can be used to distinguish between diffusion- and desorption-controlled release.

It is thought that impurities in the lithium ceramic could affect the tritium transport rate. Impurities could alter the diffusivity by creating vacancies, interstitials, or other defects. In lithium aluminate, it has been postulated that tritium diffusion occurs via a lithium-vacancy tritium complex [35]. If this is the case, then impurities that affect the number of lithium vacancies should also affect the tritium diffusivity. The sensitivity of tritium diffusivity to these impurities depends on the number of lithium vacancies caused by the impurity relative to those defects present in the pure material. However, tritium diffusivity was observed [36,37] to follow a simple Arrhenius-type temperature dependence, with the diffusivity determined for the doped and undoped materials being the same within experimental error. This suggests that for the impurities investigated, they appear to have little or no effect on tritium diffusion in lithium aluminate over the temperature range investigated (600–1000 K).

Experimentally, it may be possible to address these difficulties simply by examining the tritium distribution within the ceramic. In the bulk, contributions from desorption are expected to be small and should be limited to the near-surface region. Therefore, the concentration gradient in the interior of the crystal should be less sensitive to the desorption rate constant, making it possible to obtain good values for the diffusion coefficient, even in the mixed diffusion–desorption regime. Isothermal anneals were performed [36] on single-crystal samples (approximately 1.5 mm dia) to determine the diffusivity of tritium in lithium aluminate. Large single crystals were used to minimize the contributions from desorption. Diffusion kinetics becomes more dominant as the crystal radius increases due to the decreasing surface area-to-volume ratio. However, the release may still be in the mixed diffusion–desorption regime, which would make obtaining the rate constants from the time dependence of the tritium release difficult. Therefore, the experimental approach was to section the sample after each anneal and determine the diffusivity from the tritium concentration profile within the sample. In addition, for a better understanding of the effects of impurities on tritium transport, the tritium profiles in pure and Mg-doped (0.3%) single-crystal $LiAlO_2$ were studied [36].

Tritium release from single-crystal lithium aluminate was modeled by assuming diffusion in the bulk with desorption occurring at the surface. The differential equations governing the tritium transport are

$$\partial C/\partial t = D(\partial^2 C/\partial r^2 + 2/r\, \partial C/\partial r) \quad \text{for } 0 < r < a. \tag{1}$$

and

$$\partial C/\partial r + kC/D = 0 \quad \text{for } r = a. \tag{2}$$

The solution for the case of a constant initial concentration C_i is given by Carslaw and Jaeger [37]:

$$C = \frac{2hC_i}{rG} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{a^2\alpha_n^2 + (ah-1)^2}{\alpha_n^2[a^2\alpha_n^2 + ah(ah-1)]} \sin a\alpha_n \sin r\alpha_n, \tag{3}$$

where C is concentration at position r, D is diffusivity, G is tritium generation rate (atom/s), $h = k/D$, k is desorption rate constant, C_i is initial concentration, a is crystal radius, r is radial position, t is time, α_n is roots of $a\alpha_n \cot(a\alpha_n) = 1 - \mathrm{ah}$.

Using the above approach, one can determine the diffusivity and desorption rate constant, given the tritium concentration at the surface, the tritium concentration at the center, and the initial tritium concentration. However, an alternative method might be to fit the total observed tritium profile to Eq. (3). This approach would minimize errors due to measuring the very small crystals left at the end of the dissolution. Diffusivity values were obtained from the initial concentration in the single-crystal $LiAlO_2$ experiments [36] (determined from the sum of the tritium collected in ethylene glycol traps during the sample anneal and the tritium remaining in the sample determined by sectioning) and a minimization routine that fits the concentration data to Eq. (3). Tritium diffusivity was observed to follow an Arrhenius-type temperature dependence, with the diffusivity determined for the doped and undoped materials being the same within experimental error. This suggests that impurities are likely to have little or no effect on tritium diffusion in lithium aluminate over the temperature range investigated (600–1000 K).

4.2. Tritium desorption from the ceramic surface

While desorption has been determined to be the rate-limiting step in tritium release [32,38,39], the details of the release process are still not well understood. Early on, tritium desorption was treated as occurring from one site with one desorption activation energy. However, in several laboratory studies [40–42], the rate of evolution of H_2O (g) from a lithium-containing ceramic was observed to go through several maxima in evolution of tritium. This behavior was interpreted as indicating that evolution proceeded from several types of desorption sites, each with its corresponding activation energy. Isotherms and isobars derived from the adsorption data revealed two processes with different activation energies for adsorption. Also, the heats of adsorption were found to depend upon the degree of surface coverage.

In developing theoretical models of tritium release from the ceramic breeder materials, the activation energy of desorption is an important variable. The activation energy for desorption is equal to the sum of the heat of adsorption and the activation energy of adsorption [43,44]. Usually, the activation energy of adsorption is small so that the activation energy of desorption is approximated by the heat of adsorption. It follows that the activation energy of desorption is a function of surface coverage, as is the heat of adsorption. The observed range of values for the heat of adsorption indicates a range of activation energies for desorption. The physical basis for such a range is the existence of multiple types of sites for adsorption, and hence, multiple types of sites from which desorption occurs [45,46]. For example, a theoretical analysis of the types of OH^- sites possible on the surface of alumina, characterized in terms of the number of O^{2-} nearest neighbors, showed five types of sites to be present.

The complexity of the H_2O (g) adsorption/desorption process for lithium aluminate has been examined [47]. Reactivity differences in adsorption sites could be that one kind of adsorption site involves lithium ions and adjacent oxides, and another kind of site involves aluminum ions and adjacent oxides. Further evidence from a number of studies on candidate ceramic breeder materials indicates that multiple types of sites, with their associated activation energies for desorption, are involved in the desorption of H_2O (g), HTO (g), or T_2 (g) from the ceramic breeder surface [45]. The degree of surface coverage by adsorption of H_2O (g) or H_2 (g) and diffusion of tritium to the grain surface will determine which type of site is dominant in the release process and what the desorption activation energy will be at that time. These processes differ in several respects: (1) they can involve chemisorption or physisorption, (2) there can be different degrees of surface coverage by OH^- groups, and (3) there can be differing types of surface sites from which desorption occurs. The distinction in sites may involve defects and impurities, as well as differences in ions on different crystallographic planes exposed to the gas phase.

A study of hydrogen adsorption/desorption from lithium oxide using a combination of temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements was carried out to gain information about the species present on the surface of the lithium ceramic and their relationship to tritium desorption [45]. From the shape and position of the desorption peak in the TPD spectra one can obtain information about the energetics of the desorption process. However, as TPD provides no information on the identity or form of the species desorbing from the surface, DRIFTS fills this gap and provides the information on the identity of surface species.

Complementary to the above are the studies of the tritium release process through various analytical means using Fourier transform infrared spectroscopy (FTIR), work function measurements, and deuterium as tracer material. In an FTIR study, the deuteroxyl group OD was directly observed on the Li_2O surface at high temperature and under controlled atmosphere. Multiple peaks were observed in the O–D stretching vibration region and exhibited varied dependence on temperature and oxygen potential of the surface [48]. Yamaki et al. [49] emphasized that tritium release from Li_2O is affected both by swamping effects with H_2 and H_2O and by the surface oxygen potential. Work function techniques were used to examine the defect structure of Li_4SiO_4 [50]. The work function was found to depend upon the oxygen potential and the defect structure in the near surface region. Irradiation defects were shown to have an impact on tritium release at low temperatures (<500 K), and this may be important for low temperature operation of the breeder blanket [51,52].

5. Quantum chemical description of ceramic surface

A better grasp of the role of hydrogen in the tritium release process may be gained through an understanding of the mechanism by which hydrogen enhances tritium release. A mathematical approach employing computer simulation technology has been used to model the processes involved in the adsorption of hydrogen onto the lithium oxide surface. The methodology is guided by ab initio calculations of hydrogen chemisorption on Li_2O surfaces. The constraints placed on the mechanistic processes by stoichiometry requirements were examined and led to consideration of both surface steps and point defects.

The technique that has been employed is the self-consistent-field Hartree–Fock method with linear combination of atomic orbitals (LCAO) modified to a crystalline environment. The ab initio method contains no ad hoc adjustable parameters and uses crystal orbitals (COs) instead of molecular orbitals (MOs) [53–55]. These COs are defined (similar to the molecular orbital approach) as a linear combination of atomic orbitals, but with the periodic environment of the crystal built-in. This approach takes the extended nature of the crystalline lattice into account. The CRYSTAL code [56] that we use for such calculations has adopted this CO approach. However, for some low symmetry configurations, such as kinks and ledges on surface step structures, the CRYSTAL approach may not be practical. In such situations, a finite cluster approach, based on the GAUSSIAN90 code [57], was found to be more suited to simulate the low symmetry configurations. Both codes have been utilized in a complementary manner. The main emphasis of the study was to investigate the possibility for dissociative hydrogen chemisorption on the unrelaxed terrace sites of Li_2O surfaces, with the CRYSTAL code being the principal tool used [53].

A slab model was also used when the semi-infinite lithium oxide crystal was simulated by a finite number of atomic layers parallel to the crystal surface. Hydrogen adsorption onto the (1 1 0) and (1 1 1) terraces of lithium oxide and the step structures on the (1 1 0) terrace have been investigated. Surface reactivity has been determined by using an analysis of the change in the local density of states (DOS) as a function of the change in the local environment.

One of the keys to a successful ab initio calculation is obtaining a good basis set to represent the electronic structure of the species. In the case of lithium oxide, its bonding characteristic is strongly ionic. In free space, the O^{2-} ion is unstable; however, in crystalline Li_2O, the anion is stabilized by the surrounding Li^+ ion environment. In this situation, the two extra electrons on the oxygen ion would induce a relaxation of the valence electrons. This particular consideration for O^{2-} is necessary for any oxide in which the bonding is reasonably ionic. This effect is taken into account in an optimized basis set designed for the oxygen ion in an Li_2O environment. Recent calculations on bulk crystalline Li_2O done by Dovesi et al. [58] have indicated that the optimized basis set, (14s/6p) and (7s/1p) for oxygen and lithium, respectively, yields lattice constants, elastic constants, and central-zone phonon frequencies in good agreement with experimental values. Table 1 lists the results of the calculations and the corresponding experimental data. We have adopted this crystalline basis set [53] for our calculations involving lithium oxide. For hydrogen, the basis set (7s/1p) obtained by Dovesi et al. [59] was used, wherein the calculated equilibrium Hartree–Fock bond length of H_2 of 0.738 Å is in good agreement with its experimental value of 0.742 Å [60].

The key to successful operation of a tritium breeder blanket is to understand the tritium transport and release characteristics and the role that hydrogen plays in this process. Indications are that grain size (surface-to-volume ratio) largely determines whether tritium release is limited by diffusion or desorption [32]. That is, the larger the grain size, the higher the probability that bulk diffusion will determine the release rate. For smaller grain size, the actions taking place on the grain surface become extremely important, especially as regards the role that hydrogen plays in the overall process. Experimental studies [20] have indicated that the presence of 0.1% H_2 in the helium purge gas enhances the release of tritium from the lithium ceramic. The tritium released has been found in the form of both HT and HTO.

Bombardment of lithium ions by neutrons creates tritium in the form of T^+. In this configuration, there are

Table 1
Comparison of the energy and geometrical parameters from Hartree–Fock calculations with experiment

	Dovesi et al. [58]	Experiment
Total energy (eV)	−2447.920	–
HF cohesive energy (eV)	7.864	11.755[a]
Lattice parameter (Å)	4.57	4.57 [61,62]
Bulk modulus (dyne cm^{-2})	0.93×10^{12}	0.85×10^{12} [61,62]

[a] Obtained from thermochemical data [63].

several ways in which tritium could escape from the surface. Under normal conditions, a chemical species will be released from a solid surface in a molecular form, such as T_2 or T_2O. At steady state and in the presence of irradiation with no hydrogen in the helium purge gas, the concentration of T^+ inside the solid is of the order of a few tens of ppm [21]. If the released form of tritium is in the form of T_2 or T_2O, the rate of release is proportional to the square of the tritium concentration in the lithium-based solid breeder material. The probability of forming T_2 or T_2O is very small, and release is slow. The slow tritium release in the absence of hydrogen in the purge gas is limited by the difficulty of forming molecular species that require two tritium atoms; this effect has been observed in both in-reactor tests and laboratory experiments.

The ab initio calculations on the dissociative hydrogen chemisorption on lithium oxide surfaces [49,53] provide one component of the quantitative basis for an understanding of the role of hydrogen in affecting the release of tritium from lithium ceramic breeders. These calculations suggest heterolytic adsorption of hydrogen onto the ceramic surface. However, the presence of hydrogen in the purge gas stream (e.g., as an additive $\sim$0.1–1% H_2) provides a very different environment. The hydrogen is chemisorbed onto the lithium ceramic surfaces forming OH^- and $Li^+H^-Li^+$. There are two possible reactions with T^+:

$$Li^+H^-Li^+ + T^+ = 2Li^+_{solid} + HT,$$

or

$$OH^- + T^+ = HTO + V_o,$$

where V_o indicates oxygen vacancy. In both tritium release processes, the rate scales as the product of the surface coverage of the chemisorbed hydrogen species and the tritium concentration. However, the rate is not well characterized, so some doubt remains as to the details of the surface interactions in the tritium release process. The hydrogen coverage is usually much larger than the tritium concentration. Therefore, the tritium release rate is proportional to the first power in the tritium concentration and not to its square, as is the case in the absence of hydrogen. This is the basic reason that the addition of hydrogen to the purge gas leads to an enhancement of the tritium release rate.

Relying on only the 'intrinsic' impurity hydrogen concentration which is present to the level of a few ppm in nominally pure helium is unlikely to be effective, since the chemisorbed hydrogen surface coverage would then be correspondingly very low. The rates of HT and HTO formation would be no better or even lower than that of T_2 and T_2O. One needs to add hydrogen to a level substantially above the 'normal' impurity level in order for it to be effective in enhancing tritium release. The present model also suggests that the tritium release rate cannot be enhanced arbitrarily by simply increasing the hydrogen partial pressure in the helium purge stream, as there is a saturation effect. This can be understood from the fact that model simulations have indicated that a majority of the surface sites (i.e., the terrace sites) are not available for hydrogen chemisorption. Only a small number of sites (such as step ledges and point defects) are favorable. Once those sites are all occupied, further increases of the hydrogen partial pressure would not be useful.

6. Conclusions

Four ceramics continue to be tested by the international fusion-blanket community. These are Li_2O, Li_2ZrO_3, Li_2TiO_3, and Li_4SiO_4. While Li_2O and Li_4SiO_4 exhibit the highest lithium atom density, they also have the highest lithium vaporization rate and greatest sensitivity to moisture. Excellent irradiation behavior and excellent tritium release for Li_2ZrO_3 specimens were observed in several worldwide irradiation tests to lithium burnups up to 10%. Activation of zirconium is a concern, though it is small in comparison to that from currently used structural materials (steels). The overall performance characteristics for Li_2TiO_3 are excellent with respect to tritium release, insensitivity to moisture, and low activation. Emphasis on low-activation materials places great importance on candidate ceramics such as Li_2O, Li_4SiO_4, and Li_2TiO_3.

The existing data base on tritium release performance and materials properties is suitable for current breeder blanket design concepts; however, irradiation testing to high burnup and high dpa (displacements per atom) levels with fast neutrons needs to be done for candidate ceramic breeder materials to ensure proper perspective on tritium release behavior and the irradiation durability of candidate materials to end-of-life. Unfortunately, international plans for long-term irradiation have been delayed by the shutdown of several fast breeder reactors. Due to the limited options for conducting irradiation experiments in fast reactors, the ceramic breeder community may have to consider the use of a mixed spectrum reactor to obtain the minimum materials data set required for designs of test blanket modules for ITER and DEMO fusion reactors. In such a case, greater attention must be given to design details like grain size and ^{6}Li enrichment to ensure an appropriate tritium production rate and uniform damage production in the specimen. Tailoring of the neutron spectrum may be an alternative way to ensure a hard spectrum, but with some loss of neutron fluence.

The ongoing irradiation program needs to give greater attention to the release characteristics of neutron-generated helium. What data are available suggest that helium releases much slower than tritium and, therefore, could cause a blanket swelling problem if helium gas cannot escape from the ceramic. In testing of candidates in small grain form, this may not represent too great a problem. However, a demonstration experiment would help define the boundary conditions for acceptable helium behavior.

In summary, the development of the properties database for lithium-containing ceramics has yet to identify a critical issue that would negate their use as tritium breeding materials in a fusion reactor. Several of the candidate materials have performed well to burnups in excess of 10% under some very demanding in-reactor conditions. Issues of current interest are reactor-relevant-scale fabrication of ceramics, thermal mechanical and thermal hydraulic behavior of blanket submodules, tritium release, tritium inventory, tritium transport/release modeling, irradiation behavior to end-of-life burnup, and displacement damage levels.

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